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**PATENT COOPERATION TREATY (PCT)
TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)**

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International Application No. }
Demande internationale n° } **PCT/IB02/05112**

International Filing Date } **04 December 2002**
Date du dépôt international } **(04.12.02)**

Geneva/Genève,

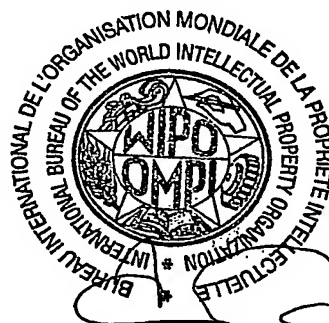
**08 December 2003
(08.12.03)**

**International Bureau of the
World Intellectual Property Organization (WIPO)**

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DOCUMENT DE PRIORITÉ

PRÉSENTÉ OU TRANSMIS
CONFORMÉMENT À LA
RÈGLE 17.1.a) OU b)



J.-L. Baron

Head, PCT Receiving Office Section
Chef de la section "office récepteur du PCT"

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

| | |
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| For receiving Office use only | |
| PCT/IB 02/05112 | |
| International Application No. | |
| (04.12.02) | 04 DECEMBER 2002 |
| International Filing Date | |
| INTERNATIONAL BUREAU OF WIPO | |
| PCT International Application | |
| Name of receiving Office and "PCT International Application" | |
| Applicant's or agent's file reference (if desired) (12 characters maximum) | |
| MOL0630-X2 | |

| | |
|---|--|
| Box No. I TITLE OF INVENTION | |
| A METHOD OF CONDITIONING IRON ALLOY-BASED ANODES FOR ALUMINIUM ELECTROWINNING CELLS | |
| Box No. II APPLICANT | |
| Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.) | |
| MOLTECH Invent S.A. 68-70 Bd de la Pétrusse 2320 Luxembourg LUXEMBOURG | |
| <input type="checkbox"/> This person is also inventor. | |
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| Teleprinter No. | |
| State (i.e. country) of nationality: LU | State (i.e. country) of residence: LU |
| This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box | |
| Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S) | |
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| DURUZ, Jean-Jacques Rue de Hesse 4 1204 GENEVA SWITZERLAND | |
| This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.) | |
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| <input type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet. | |
| Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE | |
| The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative | |
| Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) | |
| CRONIN, Brian MOLTECH S.A. Rte de Troinex 9 1227 CAROUGE SWITZERLAND | |
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| Teleprinter No. | |
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Sheet No. 2....

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

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Sandrigham House
NASSAU
BAHAMAS

This person is:

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☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

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This person is:

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This person is:

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This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (i.e. country) of nationality:

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This person is applicant for the purposes of:

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Sheet No. 3

Box No. V DESIGNATION OF STATES

Mark the applicable check-boxes below; at least one must be marked.

The following designations are hereby made under Rule 4.9(a):

Regional Patent

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Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM

Further priority claims are indicated in the Supplemental Box ☐

The priority of the following earlier application(s) is hereby claimed:

| Country (in which, or for which, the application was filed) | Filing Date (day/month/year) | Application No. | Office of filing (only for regional or international application) |
|---|---------------------------------|-----------------|---|
| item (1) | | | |
| item (2) | | | |
| item (3) | | | |

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

☐ The receiving Office is hereby requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used): ISA / EP

Earlier search Fill in where a search (international, international-type or other) by the International Searching Authority has already been carried out or requested and the Authority is now requested to base the international search, to the extent possible, on the results of that earlier search. Identify such search or request either by reference to the relevant application (or the translation thereof) or by reference to the search request:

Country (or regional Office):

Date (day/month/year):

Number:

Box No. VIII CHECK LIST

This international application contains the following number of sheets: 4^A

1. request : [2] sheets
 2. description : 14 sheets
 3. claims : 5 sheets
 4. abstract : 1 sheets
 5. drawings : sheets

Total : [23]²⁴ sheets

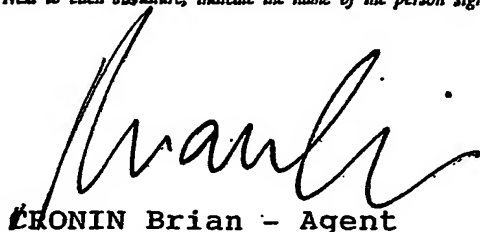
This international application is accompanied by the item(s) marked below:

1. ☐ separate signed power of attorney
 2. ☐ copy of general power of attorney
 3. ☐ statement explaining lack of signature
 4. ☐ priority document(s) identified in Box No. VI as item(s):
 5. ☐ fee calculation sheet
 6. ☐ separate indications concerning deposited microorganisms
 7. ☐ nucleotide and/or amino acid sequence listing (diskette)
 8. ☐ other (specify):

Figure No. _____ of the drawings (if any) should accompany the abstract when it is published.

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).


 CRONIN Brian - Agent

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1. Date of actual receipt of the purported international application:

03 DECEMBER 2002 (03.12.02)

3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:

04 DECEMBER 2002 (04.12.02)

4. Date of timely receipt of the required corrections under PCT Article 11(2):

5. International Searching Authority specified by the applicant:

ISA / EP

6. ☒ Transmittal of search copy delayed until search fee is paid

2. Drawings:

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A METHOD OF CONDITIONING IRON ALLOY-BASED ANODES
FOR ALUMINIUM ELECTROWINNING CELLS

Field of the Invention

5 This invention relates to the conditioning of iron
alloy based aluminium electrowinning anodes to form an
integral electrochemically active iron-based oxide layer
thereon, anodes so conditioned, aluminium electrowinning
cells with such anodes and the production of aluminium in
10 such cells.

Background Art

 The technology for the production of aluminium by
the electrolysis of alumina, dissolved in molten cryolite
containing salts, at temperatures around 950°C is more
15 than one hundred years old. This process and the cell
design have not undergone any great change or improvement
and carbonaceous materials are still used as electrodes
and cell linings.

 Using metal anodes in aluminium electrowinning
20 cells would drastically improve the aluminium process by
reducing pollution and the cost of aluminium production.
Many patents have been filed on non-carbon anodes but none
has found commercial acceptance, also because of
economical reasons.

25 US Patents 4,614,569 (Duruz/Derivaz/Debely/
Adorian), 4,680,094 (Duruz), 4,683,037 (Duruz) and
4,966,674 (Bannochie/Sherriff) describe non-carbon anodes
for aluminium electrowinning coated with a protective
coating of cerium oxyfluoride, formed in-situ in the cell
30 or pre-applied, this coating being maintained by the
addition of a cerium compound to the molten cryolite
electrolyte. EP Patent application 0 306 100 (Nyguen/
Lazouni/Doan), US Patents 5,069,771, 4,960,494 and
4,956,068 (all Nyguen/Lazouni/Doan) describe metallic
35 anode substrates which may be further covered with such an
in-situ formed protective cerium oxyfluoride layer.

 US Patent 5,510,008 (Sekhar/Liu/Duruz) discloses
an anode made from an inhomogeneous porous metallic body

obtained by micropyroretically reacting a powder mixture of nickel, iron, aluminium and possibly copper and other elements. An electrochemically active oxide-based outer portion is formed by in-situ polarisation.

5 WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804
 (Crottaz/Duruz) and WO01/42534 (de Nora/Duruz) disclose
 anodes produced from nickel-iron alloys which are surface
 oxidised to form a coherent and adherent outer iron oxide-
10 based layer whose surface is electrochemically active
 surface.

 WO01/42534 (Duruz/Nguyen/de Nora) discloses a
 nickel-iron alloy aluminium electrowinning anode with an
 openly porous electrochemically active surface produced by
 removal of iron from the surface, in particular by
15 electrolytic dissolution of iron.

 WO00/06805 (de Nora/Duruz) discloses an aluminium
 electrowinning anode having a metallic anode body which
 can be made of various alloys, for example a nickel-iron-
 copper alloy. The surface of the anode body is oxidised by
20 anodically evolved oxygen to form an integral
 electrochemically active oxide-based surface layer. The
 oxidation rate of the anode body is equal to the rate of
 dissolution of the surface layer into the electrolyte.
 This oxidation rate is controlled by the thickness and
25 permeability of the surface layer which limits the
 diffusion of anodically evolved oxygen to the anode body.

 Metal or metal-based anodes are highly desirable
 in aluminium electrowinning cells instead of carbon-based
 anodes. Usually, the anodes are pre-oxidised in an
30 oxidising atmosphere before use to produce an
 electrochemically active oxide layer thereon. In practice,
 prior to insertion into the cell, the metal-based anodes
 are usually pre-heated above the molten electrolyte to
 inhibit thermal shocks in the electrolyte and its
35 solidification when the anode is immersed.

Objects of the Invention

 A major object of the invention is to provide a
 method of conditioning an iron-based alloy anode for
 aluminium electrowinning to increase its lifetime and
40 improve its electrical conductivity during use.

Another object of the invention is to provide a method of conditioning an iron-based alloy anode to form an active anode surface that has a high electrochemical activity for the oxidation of oxygen ions for the formation of bimolecular gaseous oxygen and a low solubility in the electrolyte.

A further object of the invention is to provide a method of conditioning an iron-based alloy anode to form an integral electrochemically active oxide layer with an improved density and coherence and with limited ionic conductivity for oxygen ions and a low electrical resistance.

Yet another object of the invention is to provide a method of conditioning an aluminium electrowinning anode which is made of readily available alloys(s).

Yet a further object of the invention is to provide an aluminium electrowinning anode which is made of readily available alloys(s) and an aluminium electrowinning cell having such an anode.

Summary of the Invention

The invention is based on the observation that an integral oxide layer formed by oxidation of an iron-based alloy, in particular an iron-based alloy comprising nickel and/or cobalt, is significantly denser and more coherent when the oxidation of the iron-based alloy is carried out by polarisation thereof in a molten electrolyte under specific conditions compared to oxide layers produced by conventional oxidation in air or by polarisation in a molten electrolyte as disclosed in the prior art.

To produce such a denser and more coherent oxide layer, the anode's active surface is up to immersion into the electrolyte essentially metallic and substantially unreacted with reactive species that form ceramic compounds with metals from the iron-based alloy. Such reactive species include oxygen at or above ambient temperature or fluorine-containing gases that could contact the anode while pre-heating the anode above the cell.

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It has been found that the formation of such ceramic compounds on the iron-based alloy before polarisation in the electrolyte impairs the coherence and density of the oxide layer subsequently formed in-situ, which reduces its capacity to limit diffusion of oxygen and leads to thicker oxide layers with greater electrical resistance. It has been observed that this effect is most detrimental when the iron-based alloy is pre-oxidised before electrolysis and also when the iron-based alloy is pre-heated above the electrolyte in the fluorine-containing fumes prior to immersion into the electrolyte.

The invention relates to a method of conditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina. The metallic anode structure has initially an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds, in particular oxides and fluorides, of metals from the metallic anode structure.

According to the invention, the method comprises the ordered steps of: (a) substantially preventing the essentially metallic active surface free of said ceramic compound from reacting with any reactable species, in particular oxygen and fluorine species, until immersion into a molten electrolyte containing oxygen ions; (b) immersing into the molten electrolyte the metallic anode structure with its essentially metallic active surface free of said ceramic compounds; and (c) polarising the immersed metallic anode structure at a potential above the potential of oxidation of oxygen thereby evolving oxygen on the active anode surface and oxidising the active anode surface to form on the metallic anode structure a dense and coherent integral iron-based oxide layer which is electrochemically active for the oxidation of oxygen and which inhibits diffusion of oxygen towards the metallic anode structure.

The prevention of the metallic active surface from reacting with any reactable species, in particular oxygen and fluorine species, until immersion into a molten electrolyte can be achieved either by protecting the active surface against reaction, for instance by coating the surface with a temporary protective layer, or by avoiding exposure of the active surface to a reactive

- 5 -

environment for an extended period of time during which a significant amount of anode constituents at the active surface can react with the environment.

For instance, exposure of a cast iron-based alloy to air at room temperature for a few days would not lead to significant formation of ceramic (oxide) compounds at its surface. However, when the iron-based alloy is cast and then left unprotected in the atmosphere for a long period of time before use, for example stored several months on a shelf after casting, the surface of the iron-based alloy can become noticeably altered which has been found to reduce the anode's performances, in particular the stability, lifetime and energy efficiency. Moreover, it has been discovered that even a short exposure, e.g. a few minutes, to fluorine-containing gases while pre-heating the anode above a fluoride-based molten electrolyte has a significant deleterious effect.

As opposed to the prior art anode conditioning methods in which the iron-based alloy anodes after casting were kept unprotected until immersion into the molten electrolyte and also preferably were pre-oxidised in a high temperature oxidising atmosphere and/or pre-heated unprotected in fluorine-containing fumes above the molten electrolyte before immersion into the molten electrolyte, the method of conditioning the iron-based alloy anodes of the present invention prevents substantially any reactive interactions between the anode and the environment before immersion into the molten electrolyte.

Preferably, the method of the invention includes the step of pre-heating the metallic anode structure, prior to its immersion, to a temperature at which it can be immersed into the molten electrolyte without substantial solidification thereof. During this pre-heating step, the structure's essentially metallic active surface is maintained free of said ceramic compounds by substantially preventing the active anode surface from reacting with the environment during pre-heating before immersion. This is not the case with prior art methods, when the anodes are pre-heated without the inventive conditioning.

Protection of the active anode surface prior to immersion into the molten electrolyte can be achieved by

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covering the active surface with a temporary protective layer which is substantially impermeable to any species reactable with the active surface and which is removed prior to immersion into the molten electrolyte or
5 dissolves therein as a fugitive coating.

When the anode is pre-heated in a reactive atmosphere prior to immersion, the temporary layer should be heat stable, for instance applied from a ceramic paint, e.g. an alumina-based paint, which is stable also at high
10 temperature. Of course, a heat-stable protective coating can be used even if the anode is not subjected to a pre-heat treatment.

When the anode structure is not pre-heated in a reactive atmosphere, the temporary layer for longlasting protection at ambient temperature before use, e.g. for
15 storage, can be an organic paint or a substantially impervious wrapping, e.g. made of plastic.

The anode structure can also be pre-heated prior to immersion in an inert atmosphere that is substantially free from any species reactable with the active surface.
20 In this case, no heat stable temporary protective layer is needed during the pre-heating.

The iron-based alloy outer part may comprise one or more elements selected from nickel, cobalt, copper, molybdenum, manganese, titanium, tantalum, tungsten,
25 hafnium, vanadium, zirconium, niobium, chromium, cobalt, aluminium, silicon, carbon and the rare earth metals, in particular yttrium.

In one embodiment, the iron-based alloy outer part, consists essentially of: 45-55 weight% iron; 15-55 weight% in total of nickel and/or cobalt; 0-30 weight% copper; and 0-10 weight% in total of one or more further elements, usually selected from molybdenum, manganese, titanium, tantalum, tungsten, hafnium, vanadium,
30 zirconium, niobium, chromium, cobalt, aluminium, silicon, carbon and the rare earth metals, in particular yttrium.
35

Further suitable iron-based alloy compositions for the anode structure are disclosed in WO00/40783 (de Nora/Duruz), WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804
40 (Crottaz/Duruz), WO01/42534 (de Nora/Duruz), WO01/42536

- 7 -

(Duruz/Nguyen/de Nora), PCT/IB02/03088 (Nguyen/Duruz/de Nora) and PCT/IB02/02972 (Nguyen/de Nora).

5 The metallic anode structure can be a cast alloy. Casting can be advantageously used to produce anodes of complex shapes, e.g. specially adapted for the circulation of electrolyte. Examples of such anode shapes are disclosed in WO99/02764 (de Nora/Duruz), WO00/40781, WO00/40782 and PCT/IB02/02732 (all de Nora).

10 The metallic anode structure can be quenched and/or annealed prior to immersion into the molten electrolyte, taking care however that the anode's active surface is not exposed to an environment that can substantially react with anode constituents at the active surface.

15 The invention also relates to a method of conditioning or reconditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina, for example when the metallic anode structure has been impaired by exposure to a reactive environment before use or when the anode structure has
20 been worn during use.

Such a used or impaired metallic anode structure comprises an iron-based alloy outer part having a surface which is covered with ceramic compounds, in particular
25 oxides and fluorides, of metals from the outer part. The conditioning or reconditioning method comprises the steps of: removing substantially all ceramic compounds from the surface of the outer part to form an essentially metallic active anode surface; and then conditioning as described
30 above the metallic anode structure with its essentially metallic active anode surface free of any ceramic compounds.

A further aspect of the invention relates to method of electrowinning aluminium. This method comprises
35 the steps of: conditioning an anode structure as described above including polarising it in a molten electrolyte; and electrolysing dissolved alumina in the same or a different molten electrolyte using the conditioned anode structure to evolve oxygen thereon and produce aluminium on a facing
40 cathode.

The dense and coherent integral iron-based oxide layer of the anode structure can be further formed during electrolysis by slow oxidation of the metallic anode structure at the metallic structure/oxide layer interface.

5 Constituents of the dense and coherent integral iron-based oxide layer at the oxide layer/electrolyte interface may slowly dissolve into the electrolyte during electrolysis, preferably at a rate corresponding to the oxidation rate of the metallic anode structure at the metallic

10 structure/oxide layer interface, as disclosed in WO00/06805 (de Nora/Duruz).

As disclosed in WO00/06802 (Duruz/de Nora/Crottaz) the aluminium production molten electrolyte can comprise an amount of dissolved iron species and dissolved alumina

15 sufficient to inhibit significantly dissolution of constituents of the dense and coherent integral iron-based oxide layer at the oxide layer/electrolyte interface.

The anode can be protected against the electrolyte with a cerium oxyfluoride-based outermost coating deposited

20 and/or maintained during use, for example as disclosed in the abovementioned US Patents 4,614,569, 4,680,094, 4,683,037 and 4,966,674.

Preferably, the aluminium production molten electrolyte is maintained at a temperature below 960°C,

25 preferably between 840°C and 940°C.

The aluminium production molten electrolyte can contain NaF and AlF₃ in a molar ratio in the range from 1.2 to 2.4. The alumina content in the aluminium production molten electrolyte is usually below 10 weight%, typically

30 between 5 weight% and 8 weight%.

It is preferred that alumina-depleted electrolyte is circulated away from the electrochemically active iron-based oxide layer, enriched with alumina, and alumina-enriched electrolyte is circulated towards the

35 electrochemically active iron-based oxide layer. Such an electrolyte circulation can be achieved by following the teachings of WO99/41429 (de Nora/Duruz), WO99/41430 (Duruz/Bellò), WO00/40781, WO00/40782 and WO01/31088 (all de Nora).

Another aspect of the invention relates to an aluminium electrowinning anode structure. This structure comprises an iron-based alloy metallic outer part covered with a dense and coherent integral iron-based oxide layer obtainable by conditioning by the above described method a metallic anode structure having an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds of metals from the metallic anode structure.

Compared to pre-oxidised anodes or anodes that are pre-heated unprotected in fumes above the molten electrolyte, the anode of the invention exhibits upon use in an aluminium electrowinning cell a more protective denser and more coherent oxide layer which is thinner and more conductive, as demonstrated in the example.

The invention also relates to an aluminium electrowinning anode structure having an iron-based alloy metallic outer part with an active anode surface. Before use, the active surface is essentially metallic and free of any ceramic compounds of metals from the metallic anode structure and is covered with a temporary protection medium. This protective medium substantially prevents ceramic-forming reactions at the essentially metallic anode surface and is separable from the active surface prior to immersion into the molten electrolyte or by contact with the molten electrolyte. Usually, the temporary protection medium is removable prior to immersion into the electrolyte or soluble in the electrolyte.

The temporary protection medium may comprises one or more solid layers. Suitable solid layers comprise at least one of ceramics, such as alumina, including ceramics applied from colloids, for instance colloidal alumina precursor, such as Nyacol™ and/or Condea™, and other colloid precursors of ceramics; metals, in particular reactable metals, such as aluminium, iron, copper, chromium or yttrium, for reacting with possibly diffusing reactive gases; polymers, e.g. plastic, in particular wrapping the anode structure under vacuum or inert gas or carrying one or more of the above layer constituents. Furthermore, the temporary protection medium can comprise an inert liquid or viscous material, such as oil or grease, or an inert gas, such as nitrogen or carbon

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dioxide, for example within a polymer enclosure or wrapping around the anode structure.

5 The protective layer can comprise alumina, in particular applied from a paint or slurry, and/or a polymer. The protective layer may also contain metallic particles that trap a possible oxygen diffusion before it reaches the metallic anode surface.

10 Yet another aspect of the invention relates to an aluminium electrowinning cell comprising at least one oxygen-evolving anode structure as described above.

Preferably, the cell comprises an aluminium-wettable cathode preferably having an aluminium-wettable coating, in particular a drained cathode. Suitable, aluminium-wettable coatings are disclosed in US Patent 15 5,651,874 (de Nora/Sekhar), and PCT publications WO98/17842 (Sekhar/Duruz/Liu), WO01/42168 (de Nora/Duruz) and WO01/42531 (Nguyen/Duruz/de Nora). Suitable drained cathode designs are disclosed in US Patents 5,683,559, 5,888,360, 6,093,304 (all de Nora), 6,258,246 (Duruz/de 20 Nora), as well as PCT publications WO99/02764 (de Nora/Duruz), WO99/41429 (de Nora/Duruz), WO00/63463 (de Nora), WO01/31086 (de Nora/Duruz) and WO01/31088 (de Nora).

Detailed Description

25 The invention will be further described in the following Examples:

Comparative Example

Conditioning:

A prior art-type conditioning of an anode was carried out as follows.

30 An anode was made by pre-oxidising in air at 1100°C for 3 hour a substrate of a cast nickel-iron alloy consisting of 50 weight% nickel, 0.3 weight% manganese, 0.5 weight% aluminium, 0.05 weight% C and 49.15 weight% iron, to form a very thin oxide surface layer on the 35 alloy.

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The surface-oxidised anode was cut perpendicularly to the anode operative surface and the resulting section of the anode was subjected to microscopic examination.

5 The anode before use had an outer portion that comprised an electrolyte-pervious, electrochemically active iron-rich nickel-iron oxide surface layer having a thickness of up to 10-20 micron and, underneath, an iron-depleted nickel-iron alloy having a thickness of about 10-15 micron containing generally round cavities filled with
10 iron-rich nickel-iron oxide inclusions and having a diameter of about 2 to 5 micron. The nickel-iron alloy of the outer portion contained about 75 weight% nickel.

Underneath the outer portion, the nickel-iron alloy had remained substantially unchanged.

15 Testing:

An anode prepared as above was pre-heated unprotected in electrolyte fumes above an aluminium electrowinning cell for 20 minutes and then tested therein.

20 The cell contained a molten electrolyte at 880-890°C consisting essentially of NaF and AlF_3 in a weight ratio NaF/ AlF_3 of about 0.7 to 0.8, i.e. an excess of AlF_3 in addition to cryolite of about 24 weight% of the electrolyte, and approximately 5 weight% alumina. The
25 alumina concentration was maintained at a substantially constant level throughout the test by adding alumina at a rate adjusted to compensate the cathodic aluminium reduction. The test was run at a current density of about 0.8 A/cm², and the electrical potential of the anode
30 remained in the range of 4.2 to 4.5 volts throughout the test.

During electrolysis aluminium was cathodically produced while oxygen was anodically evolved which was derived from the dissolved alumina present near the
35 anodes.

After 24 hours, electrolysis was interrupted and the anode was extracted from the cell. The external

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dimensions of the anode had remained substantially unchanged during the test and the anode showed no signs of damage.

5 The anode was cut perpendicularly to the anode operative surface and the resulting section of the used anode was subjected to microscopic examination.

It was observed that the anode was covered with an iron oxide surface layer having a thickness of 100 to 120 micron and consisting essentially of Fe_2O_3 with less than 5
10 weight% nickel oxide.

Example 1

An anode was made of the same metals as in the comparative Example except that it has an active surface essentially metallic and free of any ceramic compounds, in
15 particular neither oxides nor fluorides, of metals from the anode's surface.

The cold anode was immersed in the molten electrolyte of a cell without prior reaction of the anode's active surface with a reactive environment, i.e.
20 with the active surface essentially metallic and free of said ceramic compounds.

The molten electrolyte was at a temperature of 880-890°C consisting essentially of NaF and AlF_3 in a weight ratio NaF/ AlF_3 of about 0.7 to 0.8, i.e. an excess
25 of AlF_3 in addition to cryolite of about 24 weight% of the electrolyte, and approximately 5 weight% alumina.

Upon immersion of the anode, the electrolyte froze around the anode which prevented electrolysis. After 10 to 15 minutes in the electrolyte, the temperature of the
30 anode had reached the melting point of the electrolyte and the electrolyte contacting the anode had molten thereby permitting electrolysis.

During the test, the alumina concentration was maintained at a substantially constant level throughout
35 the test by adding alumina at a rate adjusted to compensate the cathodic aluminium reduction. The test was run at a current density of about 0.8 A/cm², and the

electrical potential of the anode remained in the range of 4.0-4.3 volts throughout the test, i.e. about 0.2 V lower in average than in the above comparative test with a pre-oxidised and fume pre-heated anode.

5 During electrolysis aluminium was cathodically produced while oxygen was anodically evolved which was derived from the dissolved alumina present near the anodes.

After 24 hours, electrolysis was interrupted and
10 the anode was extracted from the cell. The external
dimensions of the anode had remained substantially
unchanged during the test and the anode showed no signs of
damage.

The anode was cut perpendicularly to the anode
operative surface and the resulting section of the used
anode was subjected to microscopic examination.

It was observed that the anode was covered with an iron oxide surface layer having a thickness of about 100 micron consisting essentially of Fe_2O_3 with less than 5 weight% nickel oxide and additionally an outermost layer of oxides of iron and aluminium having a thickness of about 25 micron.

The iron oxide surface layer, with pores of 3 to 5 micron, was denser than the oxide layer of the above comparative anode that had pores of 5 to 10 micron. This greater density of the oxide layer of the anode conditioned according to the invention provides a better protection for the alloy located underneath oxidation and electrolyte attack.

30 Example 2

Example 1 was repeated with a pre-heating step of the anode above the molten electrolyte prior to immersion into the electrolyte.

To prevent reaction of the essentially metallic anode surface with electrolyte fumes, the anode was covered with a protective layer of alumina applied from an alumina-based colloidal slurry.

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The colloidal slurry comprised an alumina colloid carrier consisting essentially of water and colloidal alumina particles in an amount of 20 weight% of the colloid, for example Nyacol™, and suspended alumina particles in an amount of 60 weight% of the colloidal slurry.

The anode was dipped into the slurry and allowed to dry to produce an alumina coating having a thickness of 0.6 to 1.0 mm covering and protecting the essentially metallic anode surface against reaction with the environment.

After pre-heating the protected anode for about 1 hour in the electrolyte fumes above the molten electrolyte, the anode was immersed with its alumina coating into the molten electrolyte. The protective alumina coating was dissolved almost instantaneously and normal electrolysis could start.

During electrolysis, the anode behaved like the anode in Example 2. After 24 hours, the anode was removed and examined. The anode upon use was not significantly different to the anode of Example 2.

In a variation, the protective effect of the alumina slurry can be improved by substituting half of the suspended alumina particles with suspended metallic particles, such as aluminium, iron and/or copper particles, which trap a possible oxygen diffusion before it reaches the metallic anode surface. Thus, in case the temporary protective coating is not perfectly impervious to the environment, reactive constituents of the environment will react with the metallic particles of the coating and substantially not with the metallic active anode surface.

CLAIMS

1. A method of conditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina, the metallic anode structure having initially an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds, in particular oxides and fluorides, of metals from the metallic anode structure, the method comprising the steps of:
- 5
- 10 a) substantially preventing the essentially metallic active surface free of said ceramic compound from reacting with any reactable species, in particular oxygen and fluorine species, until immersion into a molten electrolyte containing oxygen ions;
- 15 b) immersing into the molten electrolyte the metallic anode structure with its essentially metallic active surface free of said ceramic compounds; and
- 20 c) polarising the immersed metallic anode structure to form thereon a dense and coherent integral iron-based oxide layer which is electrochemically active for the oxidation of oxygen and which inhibits diffusion of oxygen towards the metallic anode structure.
2. The method of claim 1, wherein prior to immersion, the metallic anode structure is pre-heated with its essentially metallic active surface maintained free of said ceramic compounds to a temperature for immersion into the molten electrolyte.
- 25
3. The method of claim 1 or 2, wherein prior to immersion into the molten electrolyte the active surface is covered with a temporary protective layer which is substantially impermeable to any species reactable with the active surface and which is removed prior to immersion into the molten electrolyte or by contact with the molten electrolyte.
- 30
- 35 4. The method of claim 3, wherein the protective layer is heat stable.

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5. The method of any preceding claim, wherein prior to immersion, the metallic anode structure is pre-heated in an atmosphere that is substantially free of any species reactable with the active surface.

5 6. The method of any preceding claim, wherein the iron-based alloy outer part comprises nickel and/or cobalt.

10 7. The method of any preceding claim, wherein the iron-based alloy outer part comprises one or more elements selected from copper, molybdenum, manganese, titanium, tantalum, tungsten, hafnium, vanadium, zirconium, niobium, chromium, cobalt, aluminium, silicon, carbon and the rare earth metals, in particular yttrium.

8. The method of claim 5, wherein the iron-based alloy outer part, consists essentially of:

- 15 - 45-55 weight% iron;
- 15-55 weight% in total of nickel and/or cobalt;
- 0-30 weight% copper; and
- 0-10 weight% in total of one or more further elements.

20 9. The method of any preceding claim, wherein the metallic anode structure is a cast alloy.

10. The method of claim 9, wherein the metallic anode structure is quenched prior to immersion into the molten electrolyte.

25 11. The method of claim 9 or 10, wherein the metallic anode structure is subjected to an annealing heat treatment prior to immersion into the molten electrolyte.

30 12. A method of conditioning or reconditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina, the metallic anode structure comprising an iron-based alloy outer part having a surface which is covered with ceramic compounds, in particular oxides and fluorides, of metals from the outer part, said method comprising the steps of:

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- removing substantially all ceramic compounds from the surface of the outer part to form an essentially metallic active anode surface; and then
- conditioning according to any preceding claim the metallic anode structure with its essentially metallic active anode surface free of any ceramic compounds.

13. A method of electrowinning aluminium comprising the steps of:

- conditioning according to any preceding claim an anode structure including the step of polarising in a molten electrolyte; and
- electrolysing dissolved alumina in the same or a different molten electrolyte using the conditioned anode structure to evolve oxygen thereon and produce aluminium on a facing cathode.

14. The method of claim 13, wherein the dense and coherent integral iron-based oxide layer formed by said polarising step of the conditioning is further formed during electrolysis by slow oxidation of the metallic anode structure at the metallic structure/oxide layer interface.

15. The method of claim 14, wherein constituents of the dense and coherent integral iron-based oxide layer slowly dissolve into the electrolyte during electrolysis, preferably at a rate corresponding to the oxidation rate of the metallic anode structure.

16. The method of claim 13 or 14, comprising maintaining in the aluminium-production molten electrolyte an amount of dissolved iron species and dissolved alumina sufficient to inhibit significantly dissolution of constituents of the dense and coherent integral iron-based oxide layer.

17. The method of any one of claims 13 to 16, comprising maintaining the aluminium-production molten electrolyte at a temperature below 960°C, preferably between 840°C and 940°C.

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18. The method of any one of claims 13 or 17, wherein the aluminium production molten electrolyte contains NaF and AlF_3 in a molar ratio in the range from 1.2 to 2.4.

5 19. The method of any one of claims 13 to 18, wherein the concentration of alumina dissolved in the aluminium production molten electrolyte is below 10 weight%, preferably between 5 weight% and 8 weight%.

10 20. The method of any one of claims 13 to 19, wherein alumina-depleted electrolyte is circulated away from the electrochemically active iron-based oxide layer, enriched with alumina, and alumina-enriched electrolyte is circulated towards the electrochemically active iron-based oxide layer.

15 21. An aluminium electrowinning anode structure comprising an iron-based alloy metallic outer part covered with a dense and coherent integral iron-based oxide layer obtainable by conditioning according to any one of claims 1 to 10 a metallic anode structure having an iron-based alloy outer part with an active anode surface which is
20 essentially metallic and free of any ceramic compounds of metals from the metallic anode structure.

22. An aluminium electrowinning anode structure comprising an iron-based alloy metallic outer part with an active anode surface which is essentially metallic and
25 free of any ceramic compounds of metals from the metallic anode structure and which is covered with a temporary protection medium that substantially prevents ceramic-forming reactions at the essentially metallic anode surface, which medium is separable from the active surface
30 prior to or upon immersion into the molten electrolyte.

23. The anode structure of claim 22, wherein the temporary protection medium is removable prior to immersion into the electrolyte.

35 24. The anode structure of claim 22 or 23, wherein the temporary protection is soluble in the electrolyte.

25. The anode structure of any one of claims 22 to 24, wherein the temporary protection medium comprises one or more solid layers.

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26. The anode structure of claim 25, wherein at least one solid layer comprises a ceramic, such as alumina.
27. The anode structure of claim 25 or 26, wherein at least one solid layer comprises a metal, in particular a reactable metal, such as aluminium, iron, copper, chromium or yttrium, for reacting with possibly diffusing reactive gases.
28. The anode structure of any one of claims 25 to 27, wherein at least one solid layer comprises a polymer.
29. The anode structure of claim 28, which is wrapped under vacuum or inert gas in the solid polymer layer.
30. The anode structure of any one of claims 22 to 29, wherein the temporary protection medium comprises an inert liquid, such as oil or grease.
31. The anode structure of claim 22 to 30, wherein the temporary protection medium comprises an inert gas, such as nitrogen and/or carbon dioxide.
32. An aluminium electrowinning cell comprising at least one oxygen-evolving anode structure according to claim 21.
33. The cell of claim 32, comprising an aluminium-wettable cathode, in particular a drained cathode.

ABSTRACT

A metallic aluminium electrowinning anode structure has initially an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds of metals from the metallic. The anode structure undergoes a conditioning treatment that includes: substantially preventing the essentially metallic active surface free of said ceramic compound from reacting with any reactable species, in particular oxygen and fluorine species, until immersion into a molten electrolyte containing oxygen ions; immersing into the molten electrolyte the metallic anode structure with its essentially metallic active surface free of said ceramic compounds; and polarising the immersed metallic anode structure to form on the metallic anode structure a dense and coherent integral iron-based oxide layer which is electrochemically active for the oxidation of oxygen and which inhibits diffusion of oxygen towards the metallic anode structure. The metallic anode structure can be covered with a temporary protection medium, e.g. a protective layer, that prevents ceramic-forming reactions at the metallic anode surface and is separable before or upon immersion into the electrolyte.